Ideally Efficient Irreversible Molecular Gears

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Abstract

Typical man-made locomotive devices use reversible gears, as cranks, for transforming reciprocating motion into directed one. Such gears are holonomic and have the transduction efficiency of unity. On the other hand, a typical gear of molecular motors is a ratchet rectifier, which is irreversible. We discuss what properties of rectifier mostly influence the transduction efficiency and show that an apliance which locks under backwards force can achieve the energetic efficiency of unity, without approaching reversibility. A prototype device based on ratchet principle is discussed.

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Man-made engines powering our cars, trains and ships, and molecular motors powering cells and subcell units are energy transducer designed to transform chemical energy, stored in form of fuel and oxygen, into mechanical work. Both can be considered as consisting of the working unit(s) and of a gear. A gear is used in order to transform the oscillatory motion of a piston (or a kinesin molecule) $x(t)$ into a continuous directed motion $X(t) \sim vt$, or into continuous rotation $\varphi(t) \sim \omega t$. A typical gear used for technical applications is a crank-and-shaft mechanism. This gear is reversible, since the continuous rotation of the crank's axle causes the oscillatory piston's motion. The relation between x and φ corresponds to a periodic, locally invertible function. The transformation of oscillations into directed motion implies symmetry breaking, determining the direction of motion. Cranks use spontaneous symmetry breaking: here both rotation directions are possible; the actual one is determined by initial conditions. The onset of motion is hard: too small oscillations can not be transformed into a continuous rotation. Moreover, the holonomic nature of gearing transformation implies synchronization of working units, if several of them are used. Molecular motors, on the other hand, use rectifiers (such as a ratchet-and-pawl system) in which the spatial symmetry is lacking from the very beginning. Rectifiers are irreversible gears, as clearly illustrated by usual electric appliance: A diode rectifier transforms an alternating current into direct one, but, being fed with a direct current, it does not produce an alternating one, but only heat. Rectification has significant advantages compared to holonomic gearing. Thus, the soft onset of the motion allows for easy control at small velocities, and the asynchronous mode of operation is of great virtue in nanoscale cellular systems, since the synchronization of molecular-level reaction events (having stochastic, Poissonian character) is a problematic task. This property is often referred to as the ability to rectify noise [1–3].

The quality of a gear can be characterized by its energetic efficiency, i.e. by a quotient between the input energy and useful work performed, so that the question of energetics of gearing got recently much attention [4–9] within different theoretical frameworks. The energetic efficiency of a holonomic gear is unity, and the Second law of thermodynamics implies that the energetic efficiency of any other isothermal gear can not exceed this limit. On the other hand, typical efficiencies of prototype ratchets (as a rocked system of Refs. [7,8] transporting particles against constant outer potential due to the work of additive oscillating field) in quasistatic regime (guaranteeing the no-loss condition for typical thermodynamic appliances, Ref. [10]) are so poor, that one wonders, why didn't the Nature look for anther mechanism to do the work. The exception is one of the systems ("system b")) discussed in Ref. [9] which is essentially a synchronized, quasiequilibrium motor. In what follows we analyze in detail the thermodynamics of rectification and show that prototypical ratchet devices lack an important property of effective rectifiers, namely the backward locking (known from the common experience with the macroscopic ratchet-and-pawl mechanism). As we proceed to show, an ideal rectifier can perform as good as a crank, and moreover a minor variation of a simple ratchet rectifier can produce a gear whose performance is not too far from the ideal one.

Let us discuss the work produced by an isothermal system under changes of outer conditions. The mean energy of the system is given by $E = \sum_i e_i p_i$, where e_i is the energy of a (micro)state i and p_i is a corresponding probability (occupation number). The energy change is then given by

$$dE = \sum_i de_i p_i + \sum_i e_i dp_i. \tag{1}$$

In quasiequilibrium Eq.(1) corresponds to the form $dE = \delta A + \delta Q$ of the First Law of thermodynamics. Out of equilibrium, the first term still corresponds to the work of outer forces, but the second one shows some new, typically nonequilibrium, aspects.

Let us discuss a case when i can be parametrized by continuous phase space coordinates $\mathbf{r} = (\mathbf{x}, \dot{\mathbf{x}})$. In an overdamped situation (typical for biological systems) the kinetic degrees of freedom decouple from spatial ones, $p(\mathbf{r}) = p(\mathbf{x})p(\dot{\mathbf{x}})$, with $p(\dot{\mathbf{x}})$ being equilibrium Maxwell distribution, see Ref. [11]. Thus we can fully concentrate on the coordinate space of the system. The energy changes due to the redistribution of occupation probabilities during time dt can be expressed as:

$$\sum_i e_i dp_i = dt \int_V e(\mathbf{r}) \frac{dp(\mathbf{r})}{dt} d\mathbf{r} = dt \left[\int_V \mathbf{j}(\mathbf{x}) grad\, U(\mathbf{x}) dV - \int_{dV} U(\mathbf{x}) \mathbf{j}(\mathbf{x}) d\sigma \right] \tag{2}$$

where the continuity equation $dp(\mathbf{x})/dt + div \mathbf{j}(\mathbf{x}) = 0$ in coordinate space is used. Here $d\sigma$ denotes the surface element of the system's outer boundary. The first term represents the heat absorbed from the bath per unit time and is equal to the Joule heat taken with an opposite sign. The second, surface term describes the work (produced within the system's volume) of the currents, which are generated outside of the system. The energy balance in the system reads: $dE/dt = P_F + P_I + q$, where P_F is the power of outer forces, P_I is the power of outer currents, and q is the heat absorbed by a system from the heat bath per unit time. For a device acting periodically or under stochastic force with zero mean $\overline{dE/dt} = 0$, so that $\overline{P_F} + \overline{P_I} + \overline{q} = 0$. Depending on the particular arrangement, the input work and the useful work of a gear can be differently distributed between P_F and P_I. On the other hand the mean heat is always dissipated, $\overline{q} < 0$.

As an example let us consider a typical electrical arrangement consisting of an outer a.c. source of voltage $U_F(t)$, of a rectifier, and of an accumulator (maintaining a constant voltage ΔU) switched in series, see the insert in Fig.1. If a thermodynamic appliance achieves ideal efficiency, it typically achieves it in quasistatic regime, since a finite-velocity mode of operation is inevitably connected with losses, Ref. [10]. Confining ourselves to a quasistatic situation, we can describe a rectifier by a Volt-Amper characteristics (load-current characteristic, LCC) $I(t) = I(U(t))$: The state of the whole system is characterized by the current $I(t)$ being the function of U, the potential difference at the rectifier. The useful work (charging the battery) is produced by the outer currents flowing against the batterie's voltage, so that its value per unit time is $P = -P_I = -\Delta U I(t)$, and the Joule heat $Q = -q = U(t)I(t)$ is uselessly dissipated. The energy balance discussed before corresponds to a Kirchhoff's law $U(t) = U_F(t) + \Delta U$. The efficiency of a rectifying device is given by: $\eta = \overline{P}/\overline{P_F} = -\overline{P}/(\overline{P} + \overline{Q})$. Hence,

$$\eta = -\overline{I(t)} \Delta U / \overline{I(t) U_F(t)}. \tag{3}$$

Note that Eq.(3) is valid for any one-dimensional rectifying device where the energy input takes place through the work of the outer forces, the useful work is produced against the constant field (by pumping particles uphill) and the Joule heat is dissipated, cf. Refs. [6–8,12]. We get:

$$\eta = -\overline{I(\Delta U + U_F(t))}\Delta U / \overline{I(\Delta U + U_F(t))U_F(t)} \tag{4}$$

Applying Eq.(4) to a system rectifying sinusoidal outer field $U_F(t) = U_0 \sin \omega t$ one gets after the change of variable $x = \sin \omega t$:

$$\eta = -\frac{\int_{-1}^{1} dx\ \xi I\left(U_0(x+\xi)\right)/\sqrt{1-x^2}}{\int_{-1}^{1} dx\ xI\left(U_0(x+\xi)\right)/\sqrt{1-x^2}}, \tag{5}$$

where $\xi = \Delta U/U_0$. In order to understand what property of the system is important for achieving high efficiencies let us discuss a hypothetical appliance with a piecewise-linear LCC

$$I(U) = \begin{cases} g_+ U & \text{for } U > 0 \\ g_- U & \text{for } U < 0 \end{cases}, \tag{6}$$

for which Eq.(5) can easily be evaluated analytically. The behavior of η for $U_0 = 0$ as a function of the outer potential ΔU is shown in Fig.1 for different values of the backward conductivity g_-. The larger is the backward resistance, the larger maximal efficiency is achieved. For $g_- \to 0$ the maximal efficiency of a gear tends to 1, and is attained for $\Delta U = U_0$. In this case the rectifier is always switched in its backward direction (locked) so that the stalling case is essentially a no-current one. Thus, if for an irreversible mode of operation, the stalling condition corresponds to vanishing of the currents, the losses are suppressed and the ideal efficiency is reached. This finding can be compared with the results of Ref. [13], where the Carnot efficiency is achieved by a heat engine built of the two ideal diode rectifiers at different temperatures.

Let us now turn to another question: how to build an appliance based on a ratchet principle, whose efficiency tends to unity under idealized conditions. We confine ourselves to a quasistatically operating systems as only candidates for potentially ideal performance. The rocked one-dimensional ratchet performs badly, because its nonlinearity is too weak. The LCC of a ratchet rectifier can be obtained by using an adiabatic solution, Refs. [1,7,8], and leads to practically linear behavior at larger voltages of both signs, showing thus no locking behavior. As we have seen, locking is important for achieving high efficiencies. We also note that the phase space of a genuine ratchet-and-pawl appliance (showing locking) is at least *two-dimensional* [14].

Many typical ratchet appliances, discussed in the literature, can be considered as special cases of a generic two-dimensional ratchet model with two impenetrable saw-tooth boundaries in a homogeneous outer field (see Fig.1a) which we call an oblique rectifier. Standard one-dimensional models correspond to the case when only a narrow current channel between the boundaries is present. The system works as a rocked ratchet if only the $x-$component of the field oscillates, and as a flashing appliance when only the y-component changes. The weakness of corresponding nonlinearities is connected with the fact that the number of the particles in a current channel does not depend on the field. On the other hand, the system with broad channel in an oblique field can reach very high efficiencies due to locking.

Note that an oblique rectifier in homogeneous outer field $\mathbf{F}$ can be described by a LCC: In homogeneous field one has $Q = \int \mathbf{jF} dV = \mathbf{F} \int \mathbf{j} dy dx$. Due to conservation $\int \mathbf{j} dy = I$ so that $Q = I\mathbf{F} \int dx = IU$, where U is the potential difference between the leftmost and the rightmost cross-sections of system. On the other hand, $P = I\Delta U$ per definition.

In what follows we don't attempt to discuss in detail the LCC of a generic oblique appliance, and present only a qualitative discussion. In an oblique field the appliance can effectively be considered as consisting of the effective current channel and the trapping pockets. Fig.2b) shows a cartoon corresponding to this strongly simplified picture. The current flowing through the channel is proportional to the x-component of the outer field F and to the concentration $n(F)$ of particles in the channel, $I = \mu S F n(F)$. Here S is the channel's cross-section and μ is the particles' mobility. The concentrations of the particles in a channel and at the opening of the neck connecting it with the pocket are equal; the particle's concentration in the pocket (having the typical energetic depth $\Delta u = -Fd$, where d is the distance form the neck to the pocket's body) is $n_p(F) = n \exp(\Delta u/kT)$. Since the overall number of particles per rectifying unit is field-independent, one has $n(F)\left[\Omega_c + \Omega_p \exp(Fd/kT)\right] = n_0(\Omega_c + \Omega_p)$, where Ω_c and Ω_p are the volumes of the channel and the pocket, respectively and n_0 is the concentration in the absence of the outer field. From this the form of the LCC follows as:

$$I(U) = \frac{g_0 U}{1 + a \exp(-U/U_T)}. \tag{7}$$

Here $g_0 = \mu n_0 S(1 + \Omega_p/\Omega_c)/l$ is the zero-field conductivity, $U_T = kT/d$ is the characteristic field and $a = \Omega_p/\Omega_c$. For strong positive fields the behavior of the appliance is linear. For strong negative fields, the particles get trapped in pockets, and the current through the appliance decays exponentially. Thus the generic locking behavior shows up. Numerical evaluation of Eq.(5) using the LCC Eq.(7) leads to results shown in Fig.3. Here we plot $\eta(\Delta U)$ as a function of $\Delta U/U_0$, for the fixed values of $g_0 = a = U_T = 1$ and for the values of U_0 equal to 1, 3, 10 and 30. We note that the maximal efficiency grows with U_0 (for $U_0 = 30$ maximal value of efficiency exceeds 90%), and the position of this maximum shifts to the left, i.e. to the values ΔU approaching $-U_0$. The reason for the growth of efficiency is the fact that typical reverse differential resistance grows exponentially with U, and in the limit of strong outer fields tends to the ideal limit of 1.

In summary, irreversible gears have considerable advantages when compared with reversible ones. They allow for an asynchronous mode of operation, of great virtue for biological systems, since distinct reaction events can hardly be synchronized on molecular level. We have shown that irreversibility does not put any limits on the efficiency of energy transduction, i.e. that an ideal rectifying appliance can reach the efficiency of 1. The property important for the effective rectification is locking under backwards load. We show that small modifications of a generic ratchet system (an oblique rectifying appliance) lead to systems whose efficiency tends to this idealistic limit.

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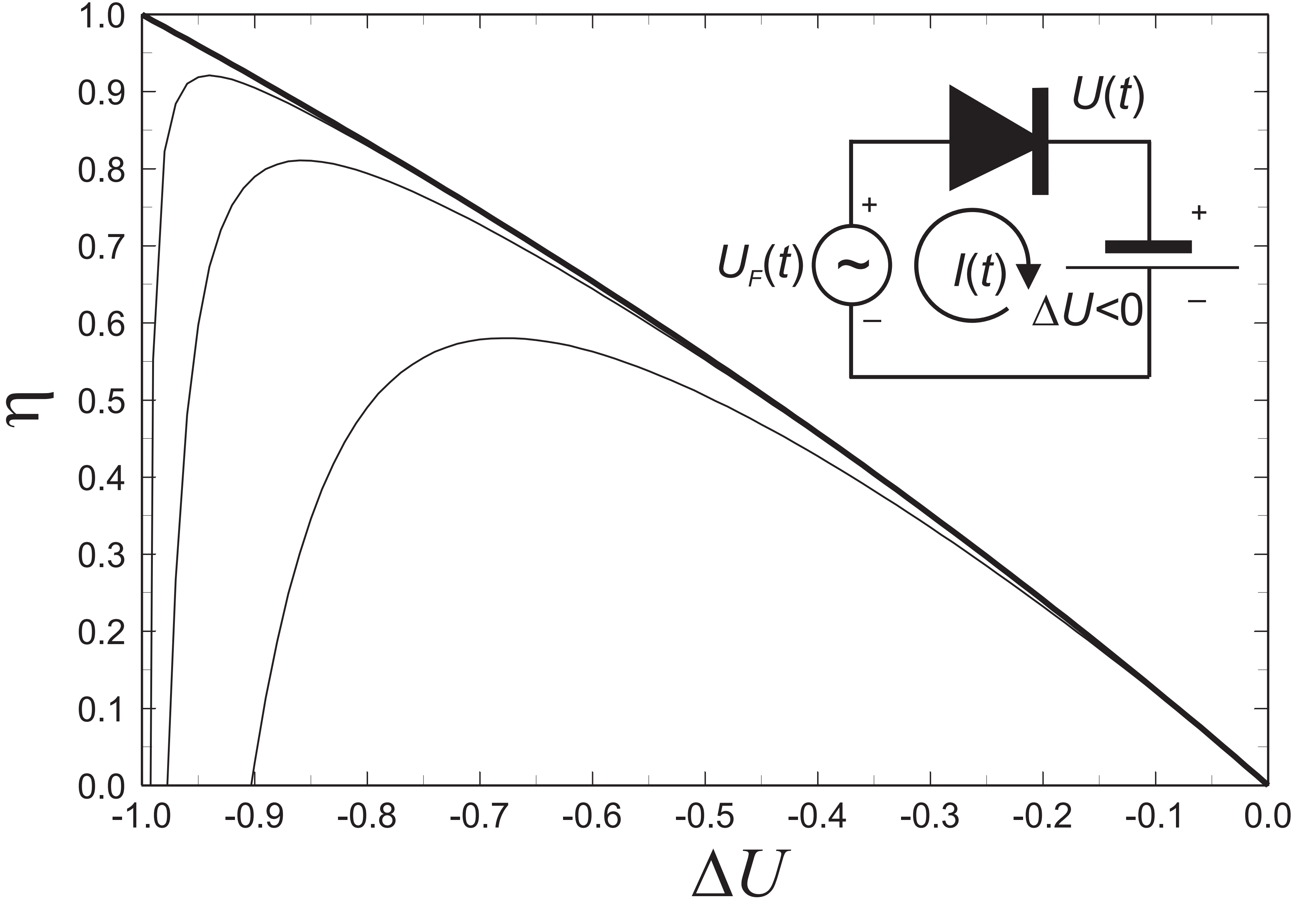
Figure Captions

Fig.1. The efficiency of a rectifier with LCC, Eq(6) switched according to a scheme shown as an insert. The battery is charged when $\Delta U < 0$. The fat line corresponds to an ideal appliance with $g_- = 0$. Three other curves correspond to $g_- = 10^{-4}$, 10^{-3} and 10^{-2}, respectively.

Fig.2. a) The oblique rectifying appliance, see text for details. When the outer field is strong enough the particles get trapped between the saw-teeth. The trapping potential is proportional to the outer field F. b) The cartoon of the appliance in fig. a), used in our considerations: this simplified version consists of the current channel and the pockets, where the particles get trapped if the outer field shows in reverse direction.

Fig.3. Efficiency of a trapping rectifier as a function of $\Delta U/U_0$ at different values of outer field amplitude U_0. Note that at larger fields the maximal efficiency tends to unity due to locking.



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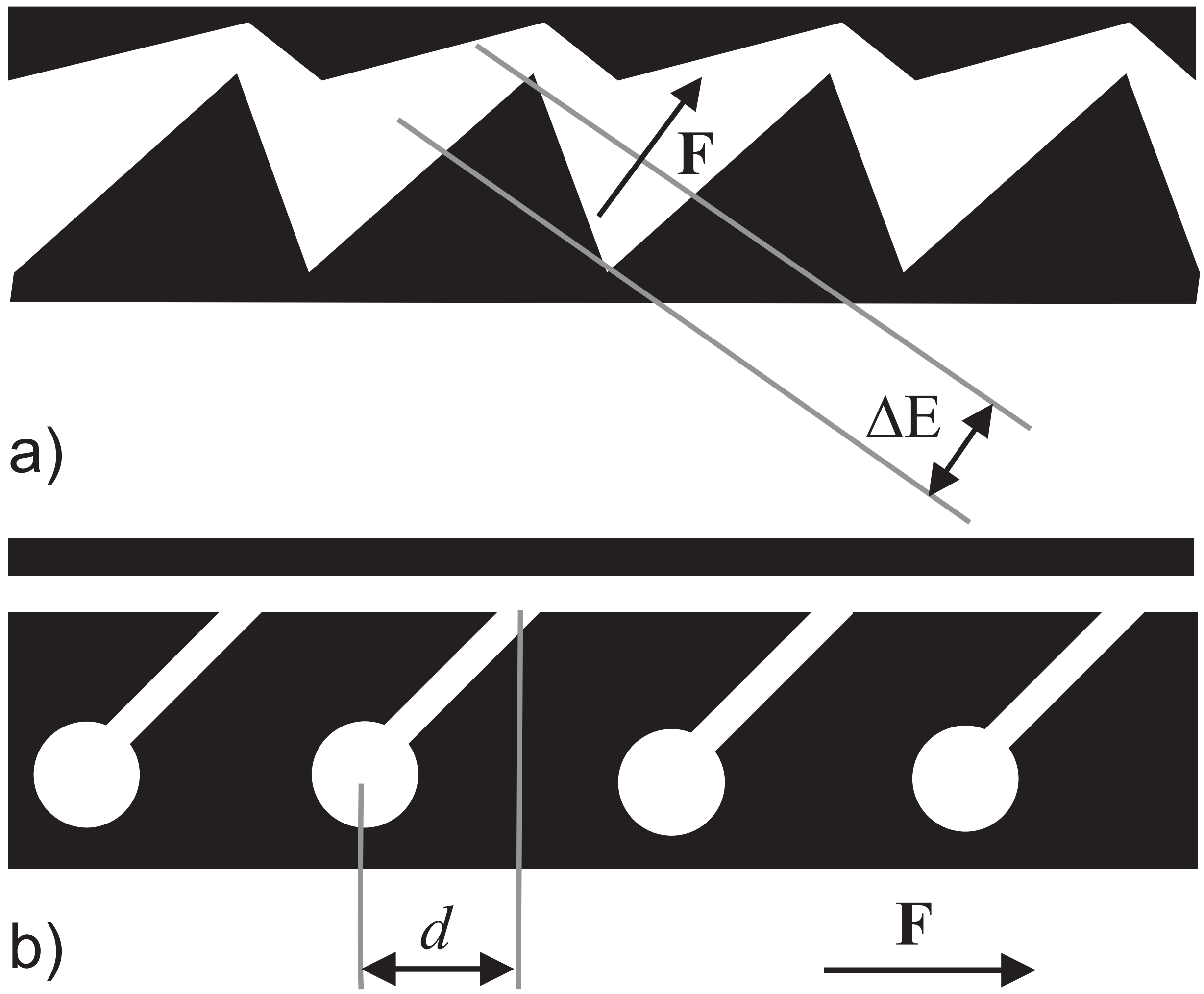
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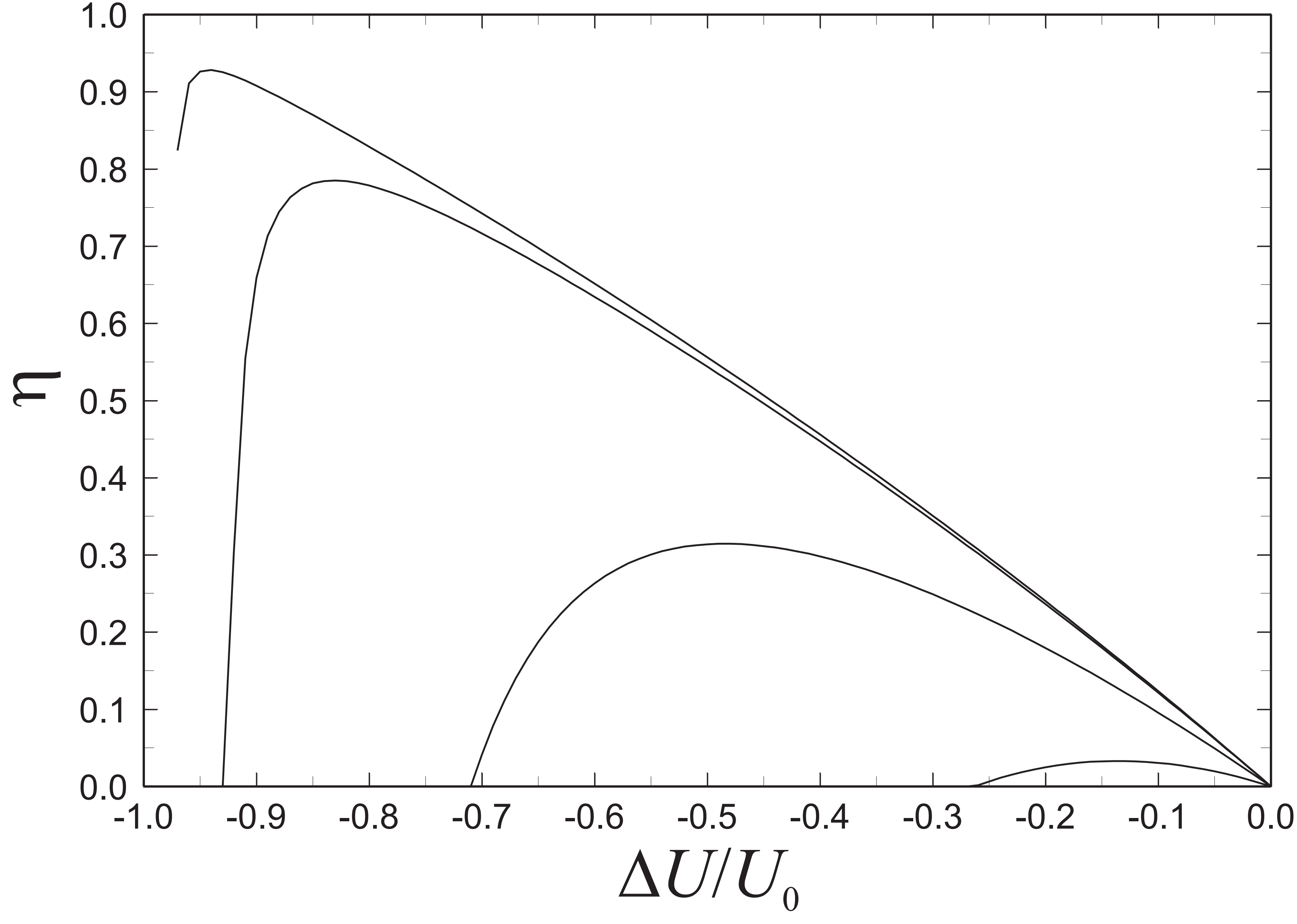

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